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“PROCESS FOR PRODUCING AMMONIUM POLYTHIOMOLYBDATE”

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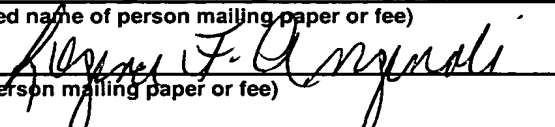
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PROCESS FOR PRODUCING AMMONIUM POLYTHIOMOLYBDATE

BACKGROUND OF THE INVENTION

5 This invention relates to a process for producing an ammonium polythiomolybdate or a hydrate thereof of the formula $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n \text{H}_2\text{O}$. More particularly, it relates to a process for producing ammonium polythiomolybdate which can be carried out economically on a commercial scale.

10 Ammonium polythiomolybdate has found use as a precursor in the preparation of molybdenum dithiocarbamate additives for lubricants.

 U.S. Patent 3,764,649 discloses the preparation of ammonium polythiomolybdate of the formula $3\text{MoS}_4 \cdot 2\text{NH}_4\text{OH}$ by reacting an aqueous ammoniacal solution of ammonium molybdate and ammonium polysulfide at 175–
15 220°C and 300–700 psig. U.S. Patent 4,604,278 teaches the production of ammonium tetrathiomolybdate by reacting an ammoniacal molybdate solution with hydrogen sulfide gas in a closed system.

20 Heretofore, the process commercially practiced for making ammonium polythiomolybdate has involved the use of ammonium sulfide which results in the formation of ammonium thiosulfate as an undesired impurity which must be removed.

 Therefore, a simpler process for producing ammonium polythiomolybdate economically on a commercial scale and which avoids thiosulfate formation would be
25 highly desirable and an advancement in the art.

SUMMARY OF THE INVENTION

30 In accordance with the present invention there has been discovered a process for producing an ammonium polythiomolybdate or a hydrate thereof of the formula $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n \text{H}_2\text{O}$ where n is 0, 1 or 2 comprising:

- 5 (a) reacting an aqueous ammoniacal molybdate solution with hydrogen sulfide gas at superatmospheric pressure, preferably 5-50 psig, for about 1 to 6 hours or until the hydrogen sulfide is no longer absorbed by the solution, said solution and said gas being in a closed system and the flow of said gas being regulated at an elevated pressure to form a slurry consisting essentially of a solid essentially all of which is ammonium tetrathiomolybdate containing a portion of the starting molybdenum and a mother liquor containing the balance of the molybdenum;
- 10 (b) heat soaking the reaction product of step (a) in the presence of elemental sulfur at elevated temperatures up to about 200°C, preferably about 175-200°C., in a closed reactor at a pressure of about 600-1000 psig whereby the ammonium tetrathiomolybdate is converted to
- 15 $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n \text{H}_2\text{O}$;
- (c) cooling said slurry to ambient temperature;
- (d) separating said solid from the major portion of said mother liquor;
- 20 (e) washing said solid with water followed by removing the resulting water washes to remove the remaining portion of said mother liquor and soluble impurities from said solid; and
- 25 (f) drying the resulting washed solid at ambient temperature to form the final $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n \text{H}_2\text{O}$, n being 0, 1 or 2, which is preferably $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13}$.

DETAILED DESCRIPTION OF THE INVENTION

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For a better understanding of the present invention, together with other and further objects, advantages, and capabilities thereof, reference is made to the

following disclosure and appended claims in connection with the above description of some of the aspects of the invention.

5 The starting source of molybdate in the process of this invention is an ammoniacal ammonium molybdate solution comprising ammonium polysulfide, which is a mixture of $(\text{NH}_4)_2\text{S}$ and elemental sulfur, S_8 , and in which solution the raw material source of molybdenum may be MoO_3 , $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ or $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. Molybdenum concentration may be 5 to 300 grams of Mo per liter.

10 The aqueous ammoniacal molybdate solution is reacted in a closed system with hydrogen sulfide gas, the flow of the gas being regulated at an elevated pressure of about 5 to about 50 psig for about 1 to 6 hours, to form a slurry consisting essentially of a solid essentially all of which is ammonium tetrathiomolybdate containing a portion of the starting molybdenum and a mother liquor containing the
15 balance of the molybdenum. The length of time of the gassing procedure depends on the size of the reaction vessel, the amount of molybdenum charged, and the actual pressure of the hydrogen sulfide gas.

20 The reaction is done in a closed system. Therefore only the hydrogen sulfide which is absorbed and reacted will be drawn off the source of the gas, therefore no gas is wasted. A gas regulator on the hydrogen sulfide gas line maintains the pressure inside the sealed reaction tank at the desired pressure. As the hydrogen sulfide is used up by the reaction to form the ammonium tetrathiomolybdate, the pressure inside the tank is effectively decreased. This causes the hydrogen sulfide gas regulator to allow
25 more gas into the tank until the pressure stabilizes at the desired pressure. As the hydrogen sulfide is reacted more is admitted to the reaction tank. Since the reaction to form the ammonium tetrathiomolybdate is exothermic, the temperature will be elevated by about 20°C to about 30°C during the reaction. When the temperature begins to drop, it indicates that the reaction has reached completion. The contents of
30 the reaction tank have therefore reached equilibrium and the flow of the hydrogen sulfide gas stops.

Elemental sulfur may then be added to the resulting slurry which is then heat soaked at preferably 175-200°C and at a pressure 600-1000 psig whereby the oxidation state of the molybdenum is changed and the ammonium tetrathiomolybdate is converted to the desired ammonium polythiomolybdate of the formula
5 $(\text{NH}_4)_2\text{Mo}_3\text{S}_{13} \cdot n \text{H}_2\text{O}$.

The slurry is then cooled to room or ambient temperature, or at least to 60°C.

10 The solid is then separated from the major portion of the mother liquor by any standard method with the preferred method being filtration. The solid ammonium polythiomolybdate is water washed and the crystals are vacuum dried to a temperature of no greater than 35°C. The mother liquor and wash water are recycled back into the process.

15 The process of this invention offers several advantages: multiple processing steps are eliminated, lower amounts of by-products are formed, more mother liquor is recycled to the process, thereby reducing disposal costs, the amount of water wash solution is reduced, and there is a higher product yield of ammonium polythiomolybdate.

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EXAMPLE

This novel process requires the reaction to be conducted in a high pressure vessel. The raw materials can all be charged into a single reactor or the MOX
25 (molybdic oxide) powder can be premixed in a separate vessel along with the ML (mother liquor) and then charged into the main reactor (pre-charging the MOX with ML and mixing for 30-60 minutes saves cycle-time). After the charges are complete into the main reactor, the reactor is closed up, purged with inert gas (N_2) and hydrogen sulfide gas is fed to the reactor. A pressure between 25 psig and 50 psig is
30 maintained while applying cooling water to the reactor jacket and/or coils. Once the exotherm is complete, H_2S feed is stopped and the contents are heated up. The pressure in the reactor increases with the vapor pressure of the contents as the temperature goes up. The reaction mass is heat soaked and then cooled. Once the

batch is completed and cooled down, the solids are recovered by filtration and then dried. It can then be directly dropped/package into super-sacks after confirming the material is dry. See table below for sequence and cycle-times.

5 **CHARGES TO THE REACTOR:**

The following charges using ML recycling yield about one metric ton ATM (ammonium polythiomolybdate product) per batch.

Molybdic oxide	1,250 lbs
Ammonium Polysulfide solution (20% sulfide content as H ₂ S and 22% NH ₃ content) (APS)	3,000 lbs
Sulfur (industrial grade dry sulfur)	600 lbs
Mother Liquor recycle; Mother Liquor has 4.5-5.5 wt.% ammonia and 8-9 wt.% H ₂ S in the aqueous solution	9,375 lbs
H ₂ S	~800 lbs
Yield (Dried ATM)	2,200 lbs
Drying losses	~300 lbs
ML purged	3,180 lbs

10 The first batch will obviously have no starting Mother Liquor. Ammonium polysulfide should be charged in its place. On subsequent batches, most of the filtrate or ML is used to dissolve the necessary amount of molybdic oxide reactant. This solution is combined with the fresh ammonium polysulfide to make-up the new reaction solution.

15 The following is a conservative estimate of the cycle times for individual steps of the ATM process:

Process Step	Cycle Time, hrs.
a. Charge MOX/ML pre-mixed solution to reactor vessel	0.5
b. Charge APS to reactor	1.0
c. Purge reactor with inert gas (to scrubber)	0.5
d. Add H ₂ S to the reactor. Maintain a pressure of 25-50 psig	4.0
e. Heat-up to reaction temperature of 180°C to 200°C	3.0
f. React at 180°C to 200°C	3.0
g. Cool to filtration temperature of < 50°C	4.0
h. Transfer to filter	1.0
TOTAL CYCLE TIME IN REACTOR	17.0
i. Filtration	4.0
j. Drying/packageging	3.0